

945.675



PATENT SPECIFICATION

DRAWINGS ATTACHED

945.675

Date of Application and filing Complete Specification: Aug. 22, 1960.

No. 28929/60.

Application made in Germany (No. B54508 IVb/22b) on Aug. 22, 1959.

Complete Specification Published: Jan. 8, 1964.

© Crown Copyright 1964.

Index at acceptance:—Classes C4, P(D1C, F); B5, B2B2; C1, H6; C3, F(2G, 2J, 3A, 3E, 3J); C3, P(4C8B, 4C10, 4C14A, 4D3B1, 7C10, 7D1A, 7D2A1, 10C8B, 10C20D1, 10C20D3, 10D1A, 14C10, 14D2F, 14D3C1, 14K7); C3, Q5X; C3, R(1C14, 2C14, 3C4, 3C9, 3C12, 3C14, 7C2, 7C9, 7C12, 7C14, 31D2E, 33C14); C4, A(9B, C4, C6A, C14); D1, B2X3.

International Classification:—C 09 b (C 04 b, C 08 b, c, f, g, C 09 d, D 01 f, D 06 p).

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are DR. WERNER DEUSCHEL, DR. FRIEDRICH GUNDEL, DR. HANNS WUEST and DR. EWALD DAUBACH, citizens of Germany and residents, respectively, of 1 Huettenuellerstrasse, Ludwigshafen/Rhein, Germany, 27 Freinsheimer Strasse, Ludwigshafen/Rhein, Germany, 169 Sternstrasse, Ludwigshafen/Rhein, Germany and 3 Haendelstrasse, Ludwigshafen/Rhein-Oppau, Germany.

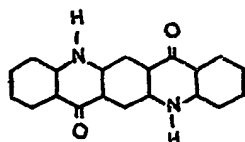
COMPLETE SPECIFICATION

A New Quinacridone Pigment Modification and Pigmented Systems obtained therewith

We, BADISCHE ANILIN-&-SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we

5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 Three modifications of 7,14-dioxo-5,7,12,14-tetrahydroquinolino-(2,3-b)-acridine (linear-transquinacridone):—



are known, which are designated as alpha-, beta- and gamma-modifications. These modifications are suitable as red pigment dyes. They have good fastness, but their shades are bluish red and violet and brilliance and hiding power leave much to be desired. There was therefore the problem of finding a red pigment dye which would have the yellowish red shade especially desired in many cases. Such a yellowish-red pigment dye must also have good general fastness, high tinctorial strength and good hiding power.

25 The object of this invention is a yellowish-

red pigment dye of the quinacridone series which has good fastness, high purity of shade, superior hiding power and high brilliance.

This yellowish-red pigment dye is a new form of the gamma-modification of linear-trans-quinacridone whose physical characteristics are three powerful lines in the X-ray diffraction pattern at a double glancing angle of 6.5°, 13.7° and 26.4°, three medium lines at 13.1°, 13.3° and 23.8° and three weak lines 17.0°, 20.5° and 25.0°. With pigments of the new form there are achieved a mean primary particle size of more than 0.1 micron, preferably 0.3 to 0.7 micron, and a specific surface of less than about 30 square metres per gram, preferably about 20 square metres per gram, pigmented systems of excellent brilliance, high colour fastness and excellent hiding power. It is above all the excellent purity of shade and especially the more yellowish tinge of the new form which surprise the observer when comparing it with the known form of the gamma-modification which is duller in shade. Comparison of the X-ray patterns and infra-red spectra of the two forms similarly reveals clear differences, even when their particles are present in the same order of magnitude.

In X-ray diffraction patterns (compare Figure I of the accompanying drawing which reproduces the X-ray spectrum of the old form of the gamma-modification with Figure II which reproduces the X-ray spectrum of the new form of the gamma-modification) there is

at a double glancing angle $D = \theta$ of 23.8° in the new form a line of medium intensity and in the old form a line of weak intensity and conversely at 25.0° in the new form a line of weak intensity and in the old form a line of medium intensity. The new form moreover has two lines of medium intensity at 13.1° and 13.3° and a line of high intensity at 13.7° . In contrast, the old form has in this range only a line of medium intensity at 13.2° and a line of high intensity at 13.8° . In the infra-red spectrum of the new form there is, in contrast with the old form, no line at 13.35 microns. The new form is therefore not merely a pigment with improved properties, but a new pigment which is characterized by a yellowish red shade, hiding power, good general fastness, above all excellent fastness to light and weathering, and resistance to high temperatures. It is not attacked by solvents or softeners.

Pigmented systems which contain the new pigment as a component of mixtures of substances, possibly in addition to other components, include pigment concentrations for colouring and coloured material ready for use, namely: pastes, flush pastes, preparations such as printing colours, distempers, binder colours or lacquers and varnishes of all kinds, such as physically and oxidatively drying lacquers and varnishes, acid, amine and peroxide curing varnishes or polyurethane varnishes. The pigment may also be used to colour synthetic, semisynthetic or natural macromolecular substances, such as thermoplastic resins, e.g., polyvinyl chloride, polystyrene, polyethylene, polyesters, phenoplasts, aminoplasts and rubber. The pigment may also be mixed with natural, regenerated or synthetic fibres, such as glass, silicate, asbestos, wood, cellulose, acrylcclulose, polyacrylonitrile, polyester, polyurethane and polyvinyl chloride fibres or mixtures of the same, and also in powders, for example organic or inorganic pigments, rock flour, cements, plaster of Paris, starches and wood flour. With the new pigment there are obtained prints, paint and varnish coatings, coverings, shaped articles, such as sheets, threads, plates, blocks, granulates and rods with a brilliant red colour of excellent durability.

The mixtures of substances which contain as active colouring ingredient the extremely brilliant yellowish-red new pigment of good hiding power, may be of solid, elastic, pasty, viscous, mobile or thixotropic consistency. They may be obtained by conventional methods. Aqueous pastes may be obtained for example by stirring the pigment into water, possibly with the addition of a wetting or dispersing agent or by stirring or kneading the pigment into a dispersing agent in the presence of water and possibly of organic solvents or oils. These pastes may for example be used for the production of flush pastes, printing colours, distempers, plastic dispersions and spinning solu-

tions. The pigment may also be introduced by stirring, rolling, kneading or grinding into water, organic solvents, non-drying oils, drying oils, lacquers, varnishes, plastics or rubber. Finally, it is also possible to work up the pigment by dry mixing with organic or inorganic masses, granulates, fibrous materials, powders and other pigments, to form mixtures of substances. The pigment dye according to this invention may obviously be used in conjunction with other pigment dyes or soluble dyes. It is moreover eminently suitable for textile printing.

In addition to its excellent hiding power, outstanding purity of shade and good general fastness, such as fastness to light and weathering and solvent and softener resistance, the new pigment is also characterized by superior resistance to high temperatures. For example, in contrast to the modifications hitherto known, the thermal behaviour of the new pigment makes it possible to work it into polyamides, for example to spin it therewith, without the shade of colour being dulled by the effect of the temperature during working up. The superiority of the new pigment in hiding power and purity of shade is also shown for example in automobile finishes; to achieve the same hiding power, a smaller amount of the new product is required than of the known gamma-modification of quinacridone. The white blend of the new pigment with titanium dioxide moreover exhibits a purer shade of colour.

The new pigment may be prepared by various methods. As initial material a quinacridone is used which is as pure as possible and which has been prepared for example by ring closure of 2,5-dianilinoterephthalic acid in polyphosphoric acid. Although the quinacridone starting material to be used for the preparation of the pigment modification having the X-ray diffraction pattern as shown in Figure II may be prepared by various methods reference is made to United Kingdom Patents Nos. 808,052 and 868,360.

For complete conversion of the resultant conventional alpha, beta and gamma modifications into the new form, these are, for example, dissolved in 5 to 20 times the amount of sulphuric acid, poured into or diluted with water or an alcohol, preferably a low boiling alcohol, for example methanol, ethanol, butanol, glycol or other alcohols boiling up to 200°C ., or ground, for example by the known salt milling process, possibly in the presence of solvents, such as alcohols, glycols or preferably N-methylpyrrolidone or other disubstituted carboxylic acid amides, such as dimethylformamide, or ground in such solvents without salt, in order to obtain it in a sufficiently finely divided form, that is with a mean primary particle size of less than 5 microns length. For industrial reasons, orders of magnitude of 0.1 to 2 microns in length and 0.01 to 0.5 micron in thickness are in general suit-

- able with acicular structures and of less than 0.5 micron edge length in the case of rhombic structures. By "salt milling" we understand the process of grinding dyes and pigments with or without liquids and in the presence of water-soluble inorganic salts. This process, its conditions, suitable salts and liquids are known to the expert and are published in the pertinent literature.
- Material prepared in this or any similar manner is then contacted in finely divided form, i.e. in a mean primary particle size of less than 5 microns length, with N-methylpyrrolidone until an X-ray diffraction pattern exhibits at a double glancing angle of 6.5° , 13.7° and 26.4° three powerful lines, at 13.1° , 13.3° and 23.8° three medium lines and at 17.0° , 20.5° and 25.0° three weak lines. For this purpose there are suitable amounts of N-methylpyrrolidone of from 0.1 to 50 times the weight of the quinacridone; amounts of 5 to 25 times are preferred. Depending on the amount of the N-methylpyrrolidone, the quinacridone is wetted thereby, made into a paste therewith or suspended therein. The presence of the N-methylpyrrolidone effects the formation of the desired pigment upon standing for example for 1 to 100 hours at temperatures of about 0° to 300° C. The temperature range between 10° and 205° C., especially above 150° C., is preferred. The formation of the pigment can also be promoted by aowing the mixture to boil, possibly under reduced or increased pressure. The formation of the pigment can also be accelerated by stirring, grinding or shearing. Such mechanical treatments are desirable if the application of temperatures substantially higher than room temperature are to be avoided and if the time required for complete conversion is to be diminished.
- When starting from a prepared material which is present in an especially finely divided form, such as is obtained for example by salt milling or by precipitation of the sulphuric acid solution of the quinacridone and hydrolysis of the sulphate formed, the time required for preparing the pigment is less, about $\frac{1}{2}$ to 4 hours at 200° C. If elevated temperatures are to be avoided, a material must be used which is present in this especially finely divided form. By grinding and shearing, this material can be converted into the new form within 5 to 20 hours. It shows two clearly defined medium lines at 13.1° and 13.3° and is yellowish-red.
- Conversion of quinacridone to the new red quinacridone pigment may be carried out in a preferred manner by grinding, in the presence of N-methylpyrrolidone, a water-soluble inorganic salt and an alkali, a precipitate obtainable by dissolving quinacridone in sulphuric acid and precipitating the quinacridone by means of methanol. The grinding or salt-milling procedure may be carried out, for example, for 10 to 20 hours by using the dried violet hydrolyzate of the blue sulphate which is formed by precipitation of a 5 to 10% solution of the synthesis product in concentrated sulphuric acid at about 0° to 50° C., preferably at 15° to 20° C. with 0.15 to 2 times, preferably 0.5 to 1 times the amount of methanol (with reference to sulphuric acid). The N-methylpyrrolidone is then preferably used in 0.1 to 10, preferably 0.5 to 5 times the amount of quinacridone. As water-soluble inorganic salts there may be used cheap salts, as for example sodium chloride or sodium sulphate, which are used in 5 to 20, preferably 10 times the amount of quinacridone. As alkalis, which are added with optimum result in 0.1 to 0.5 times the amount, there may be used for example alkali or alkaline earth hydroxides or carbonates. A ball mill is a suitable apparatus for this process.
- A form of the pigment which is especially valuable industrially and which is an especially brilliant yellowish red product of good hiding power is obtained when a suction filtration cake of the precipitated quinacridone obtained by dissolution in concentrated sulphuric acid and pouring into ice-water, and washed until neutral, is intimately mixed with 10 to 50 times, preferably 15 to 25 times, the amount (with reference to quinacridone) of N-methylpyrrolidone, freed from water by fractional distillation under normal or reduced pressure and then heated in the residual N-methylpyrrolidone at an elevated temperature until the mean size of the primary particles is 0.3 to 0.7 micron. A heating period of $\frac{1}{2}$ to 20 hours and a temperature of about 200° C. are favourable but a duration of about 1 to 4 hours is preferred. During this process, part of the N-methylpyrrolidone, for example a quarter or third, may be distilled off. The same especially desirable result is also arrived at when the aqueous paste of the precipitated quinacridone is first dried, pulverized and then converted with N-methylpyrrolidone in the said way into the new form; distilling off of the water is then unnecessary. An average mean primary particle size of 0.1 to 2 microns and a specific surface of about 10 to 30 square metres per gram are preferred.
- The following Examples will further illustrate this invention but the invention is not restricted to these Examples. The parts and percentages are by weight.
- EXAMPLE 1.**
- 20 parts of the yellowish red pigment obtained according to the following paragraph (a) and 20 parts of aluminium hydroxide are ground on a three-roller grinding mill in the usual way with 60 parts of linseed oil varnish. The printing colour prepared in this way yields, when used for book or offset printing, lustrous red prints with excellent fastness properties, especially very good fastness to light, and of good hiding power. Prints prepared on sheet

metal according to this process are moreover fast to pasteurization.

The pigment is prepared in the following way:

- 5 (a) 100 parts of linear-trans-quinacridone with a carbon content of at least 75% (obtained by ring closure of 2,5-dianilinoterephthalic acid in 10 times the amount of polyphosphoric acid with a P_2O_5 -content of more than 80%) are dissolved at 10° to 20° C. in 100 parts of concentrated sulphuric acid and precipitated by pouring into 8000 parts of ice-water.

- 15 The suction cake obtained by suction filtration is washed free from sulphate and taken up in 2,400 parts of N-methylpyrrolidone. The remaining water is fractionally distilled off in a nitrogen atmosphere. Then during three hours 800 parts of N-methylpyrrolidone are removed by distillation while raising the temperature to 200° C. After cooling, the remaining methylpyrrolidone is filtered off by suction and the residue is washed with 200 parts of N-methylpyrrolidone and then with methanol in water. The suction cake is dried at 100° C. and then pulverized. The new red pigment of linear-trans-quinacridone is obtained with a mean primary particle size of 0.5 micron.

- 30 (b) The same result is arrived at when the sulphuric acid solution according to (a), paragraph 1, is diluted at 15° to 25° C. with 1000 parts of methanol or is allowed to flow into this amount of methanol, the sulphate thus formed is filtered off by suction, hydrolyzed with water and dilute caustic soda solution, washed free from sulphate and the suction cake treated further as above described.

- 40 In the process of examples (a) and (b), the distilling off of the water from the N-methylpyrrolidone mixture can also be replaced by drying the neutral aqueous paste at 50° C. under reduced pressure and the pulverized quinacridone can then be treated as described with N-methylpyrrolidone.

- 45 (c) In a steel vibratory mill of 4 litres capacity 100 grams of linear-trans-quinacridone and 750 grams of N-methylpyrrolidone are ground for 10 hours in the presence of 12,000 grams of steel balls of 15 mm diameter. 50 1,650 grams of N-methylpyrrolidone are added to the ground material and 800 grams thereof distilled off at 200° C. under nitrogen. After cooling, the remaining methylpyrrolidone is filtered by suction and the residue is washed with 200 grams of N-methylpyrrolidone and 55 boiled up with 1000 grams of 10% sulphuric acid. The pigment, after having been filtered by suction, washed and dried, shows the same X-ray diffraction pattern as that obtained according to (a) or (b).

- 60 In the grinding in N-methylpyrrolidone, 1,500 grams of rock salt may be added; it is also possible to grind dry in the presence of this amount of rock salt; in both cases the desired yellowish-red pigment is obtained.

(d) 100 parts of crude linear-trans-quinacridone are dissolved at 15° C. in 1100 parts of concentrated sulphuric acid. Within two hours at 15° to 20° C., 550 parts of methanol are allowed to flow in slowly, the blue sulphate is filtered off by suction, washed with a mixture of 100 parts of sulphuric acid and 100 parts of methanol and then with water, taken up in 1000 parts of 1% caustic soda solution, heated to 80° C., filtered by suction while hot, washed neutral with water and dried. 85 parts of a violet powder are obtained. This powder is ground for 20 hours with the tenth part of sodium carbonate, 10 times the amount of N-methylpyrrolidone and 20 times the amount of sodium chloride in the presence of porcelain balls of 15 mm diameter in a vibratory mill. The contents are taken up in water, filtered off by suction and the sodium chloride is washed out completely with water. After drying under reduced pressure at 50° C., a yellowish red powder with the X-ray diffraction pattern of the new pigment is obtained.

EXAMPLE 2.

5 parts of the new pigment (for example from Example 1 (a)) are ground in a ball mill with a nitrocellulose solution which contains 10 parts of nitrocellulose (alcohol-soluble, low viscosity), 5 parts of dibutyl phthalate, and 80 parts of an ethyl alcohol/ethyl glycol mixture 9:1. A red intaglio printing colour is obtained which is suitable for the production of prints which are eminently fast to light and solvents and which do not bleed.

By appropriate modification of this Example especially by increasing the proportion of pigment, an aniline printing colour is obtained.

In an analogous way, by appropriate modification, printing pastes for other purposes, for example for textile printing and screen printing, may be obtained.

EXAMPLE 3.

100 parts of a product resulting from mixing linseed oil with the esterification product of phthalic acid and a mixture of glycerin and pentaerythritol are added to 100 parts of xylene and then 8 parts of the new pigment (for example from Example 1 (a)) are added; the mass is ground three times in a cone mill. A yellowish-red varnish is obtained which is suitable for spraygun application. Coatings thus prepared are characterized by good hiding power, brilliant shade and outstanding light fastness.

EXAMPLE 4.

2 parts of the new pigment (for example from Example 1 (b)) are mixed in a ball mill in the usual way with a varnish consisting of 9.5 parts of an ester-soluble nitrocellulose (alcohol-moist), 2.5 parts of dibutyl phthalate, 1.5 parts of benzyl butyl phthalate, 2 parts of a synthetic resin, as for example the pro-

duct obtained from cyclohexanone by treatment with sodium hydroxide, 16 parts of butyl acetate, 5.5 parts of methyl acetate and 13 parts of pure toluene. Coatings prepared with this varnish are characterized not only by their yellowish red shade, but also by good hiding power, and excellent fastness to light and overspraying.

EXAMPLE 5.

8 parts of the new pigment (for example from Example 1 (a)) are ground in a cone or ball mill into a stoving lacquer of 40 parts of coconut oil alkyd resin (40% coconut oil), 12 parts of urea formaldehyde resin, 40 parts of xylene and 8 parts of normal butanol. Varnishes may be prepared therewith which after curing by stoving are highly glossy and extremely fast to weathering and overspraying.

EXAMPLE 6.

5 parts of the new pigment (for example from Example 1 (c)) are ground by means of a cone mill into 100 parts of a drying unsaturated polyester resin free from paraffin. To the ground product there are added 10 parts of monostyrene and 1 part of cyclohexanone peroxide paste (40% in dibutylphthalate), the whole is thoroughly stirred and finally 4 parts of drier solution (10% cobalt naphthenate in white spirit) and 1 part of silicone oil solution (1% in xylene) stirred in. The mixture is applied to primed wood and a highly glossy, waterproof red coating is obtained which does not lose its brilliance.

EXAMPLE 7.

A mixture of 70 parts of polyvinyl chloride, 30 parts of di-iso-octyl phthalate and 1 part of titanium dioxide (rutile type) are coloured in the usual way with 0.5 part of the new pigment (for example from Example 1 (b)) on mixing rollers heated to 160° C. An intensely red coloured plastic composition is obtained which may serve for example for the production of sheets or sections. The coloration is characterized by outstanding fastness to light and softener.

EXAMPLE 8.

1 part of polystyrene granulate is mixed dry with 1 part of the new pigment (for example from Example 1 (c)) in a mixing drum by powerful shaking. The mixture is then homogenized with the aid of a colour extruder heated to 180° C. The string extruded from the nozzle of the extruder is comminuted on a cutting machine and the coloured granulate thus obtained is moulded in an injection moulding machine. Brilliant red mouldings are obtained having high fastness to light. Polyethylene and polycaprolactam can be coloured red in the same way.

EXAMPLE 9.

A rubber mixture of 100 parts of pale crêpe, 2.6 parts of sulphur, 1.0 part of stearic acid,

1.0 part of 2-mercaptobenzthiazole, 0.2 part of hexamethylene tetramine, 5.0 parts of zinc oxide, 60.0 parts of chalk and 2.0 parts of titanium dioxide (anatase type) is coloured in the usual way on mixing rollers at 50° C. with 2.0 parts of the new pigment (for example from Example 1 (c)) and vulcanized for 12 minutes at 140° C. An intensely red coloured vulcanizate is obtained.

EXAMPLE 10.

10 parts of the new pigment (for example from Example 1 (d)), 60 parts of titanium dioxide (rutile type), 25 parts of lithopone, 15 parts of talc are made into a paste with 30 parts of a wetting liquid (solution of 1% of sodium hexametaphosphate and 3% of a condensation product from sodium 2-naphthalene sulphonate and formaldehyde in water) and ground in a ball mill. The paste thus formed possibly while adding more water, is stirred into 100 parts of a commercial polyvinyl acetate dispersion (solids content about 55%). With the resultant binder colour, coatings which have excellent fastness to light and wet-wiping are obtained.

Instead of the polyvinyl acetate dispersion there may also be used a commercial self-vulcanizing rubber latex and by dipping suitable moulds, thin-walled rubber articles of powerful colouration can be prepared.

EXAMPLE 11.

20 parts of heavy spar are suspended with a solution of 10 parts of aluminium sulphate in 100 parts of water. Then 5 parts of sodium carbonate containing water, dissolved in 50 parts of water and 10 parts of an aqueous dye paste are stirred in which contains 20% of the new pigment (prepared from the N-methylpyrrolidone-moist suction cake from Example 1 (a) by treatment with the necessary amount of water). Finally there is added a solution of 12 parts of barium chloride in 120 parts of water, the precipitate deposited is filtered off by suction and the residue washed with water. 20 parts of the paste obtained are mixed with 4 parts of a 20% glue solution. In this way a wallpaper colour is obtained which gives wallpaper of very good fastness to light.

EXAMPLE 12.

5 parts of the new pigment (for example from Example 1 (d)) are ground in a edge-runner with 100 parts of plaster in the usual way and then adjusted with water to a readily workable mixture. After setting, a red coloured plaster is obtained.

Cement can be worked up into a red coloured concrete in an analogous way.

EXAMPLE 13.

To 100 parts of bleached sulphite cellulose in a beater there are added in the usual way 2 parts of a 20% aqueous pigment paste which

has been obtained directly from the N-methylpyrrolidone-moist suction cake according to Example 1 (a) by treatment with the necessary amount of water. Then 3 parts of wood glue and 4 parts of aluminium oxysulphate in powder form are stirred in. After grinding, the whole is worked up on a paper machine. A brilliant red material is obtained.

EXAMPLE 14.

250 parts of a 20% aqueous pigment paste which has been obtained from the N-methylpyrrolidone-moist suction cake from Example 1 (a) by treatment with water are made up to 500 parts with water and to this is added a clear solution of 15 parts of resin soap (obtained by boiling colophony with caustic soda solution in the usual way) and 150 parts of water. The suspension of the pigment is uniformly dispersed with a suitable stirrer (for example with rebound and shear action) and then at 40° C. while stirring a solution of 5 parts of calcium chloride in 110 parts of water is slowly added. After stirring for 15 minutes at 60° C., the pigment is filtered by suction at about 50° C., washed in the usual way with water and dried to constant weight at 50° C. under reduced pressure. 55 parts of a red powder are obtained which is composed of about 75% of pigment and 25% of calcium lake of the resin soap. This red powder may be dispersed especially easily in the usual pigment binding agents.

EXAMPLE 15.

120 parts of an aqueous pigment paste containing 40 parts of pure pigment from Example 1(a) and 60 parts of a condensation product from sodium 2-naphthalene sulphonate and formaldehyde have water added to make up the total mixture to 200 parts. This mixture is ground in a ball mill until the pigment has reached the desired degree of fine division. A pigment paste is obtained with a content of about 20% of the new pigment and 30% of dispersing agent, which immediately disperses in aqueous media like ink. It is especially suitable for pigmenting plastic dispersions, rubber latex, binder colours, paste colours, glues, emulsions, paper in bulk, spinnable cellulose xanthate and other aqueous media. Thus for example in Example 10, 50 parts of the above pigment paste may be used instead of the 10 parts of the new pigment. The addition of the wetting liquid is then unnecessary. The above pigment paste may also be used in Example 13.

The pigment paste may however be completely dried, for example in the air, under reduced pressure, at elevated temperature or on a roller drier, and the dry material flaked or finely ground. The pigment preparation with a content of about 40% of the new pigment and 60% of dispersing agent thus obtained behaves just like the original pigment paste described above upon the addition of water.

EXAMPLE 16.

5 parts of the pigment paste from Example 15 are stirred well with 45 parts of water. This pigment suspension is added to about 2000 parts of a spinnable cellulose xanthate solution which contains 100 parts of cellulose. After the pigment has been uniformly dispersed in the xanthate solution by stirring, the solution is spun in the usual way. Brilliant yellowish red threads of high uniformity of shade are obtained. Instead of the pigment paste, there may also be used 2.5 parts of the dried pigment preparation.

If a dispersing agent soluble in acetone is used for producing the pigment preparation, red spin-dyed acetyl cellulose fibres may be prepared in an analogous way.

WHAT WE CLAIM IS:—

1. As a pigment dye a modification of 7,14-dioxo - 5,7,12,14 - tetrahydroquinolino - (2,3-b)-acridine which exhibits three powerful lines in the X-ray diffraction pattern at a double glancing angle of 6.5°, 13.7° and 26.4°, three medium lines at 13.1°, 13.3° and 23.8° and three weak lines at 17.0°, 20.5° and 25.0°, in a mean primary particle size of more than 0.1 micron, preferably of 0.3 to 0.7 micron, and with a specific surface of less than about 30, preferably about 20, square metres per gram.

2. A process for the production of the pigment specified in claim 1 wherein 7,14-dioxo-5,7,12,14 - tetrahydroquinolino - (2,3 - b)-acridine is converted by contacting it in a mean primary particle size of less than 5 microns length with N-methylpyrrolidone until an X-ray diffraction pattern exhibits at a double glancing angle of 6.5°, 13.7° and 26.4° three powerful lines, at 13.1°, 13.3° and 23.8° three medium lines and at 17.0°, 20.5° and 25.0° three weak lines.

3. A process as claimed in claim 2 wherein the conversion is allowed to proceed at an elevated temperature, preferably above about 150° C.

4. A process as claimed in claim 2 or 3 wherein the dye used for the conversion has been precipitated from a sulphuric acid solution by means of water and/or a low boiling alcohol.

5. A process as claimed in claim 4 wherein methanol is used for the precipitation.

6. A process as claimed in claim 2 or 3 wherein the dye used for the conversion has been prepared by grinding, in the presence or absence of a water-soluble inorganic salt.

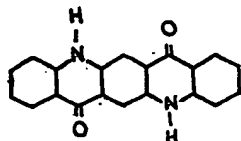
7. A process as claimed in claim 5 wherein the precipitated dye is converted by grinding in the presence of N-methylpyrrolidone, a water-soluble inorganic salt and an alkali.

8. The process for the production of 7,14-dioxo-5,7,12,14-tetrahydroquinolino - (2,3-b)-acridine, exhibiting the X-ray diffraction pattern as defined in claim 1, from other modifications of said acridine derivative substanti-

ally as described in any of the foregoing Examples.

9. Pigments when obtained by the process claimed in any of claims 2 to 8.

5 10. Any dye of the formula:—



which has been converted into a pigment form exhibiting the X-ray diffraction pattern as defined in claim 1 in the manner described in any of the foregoing Examples.

10 11. Any pigmented system, including solid or liquid substances or mixtures, which contains as pigment dye the dye claimed in either of claims 1 and 10.

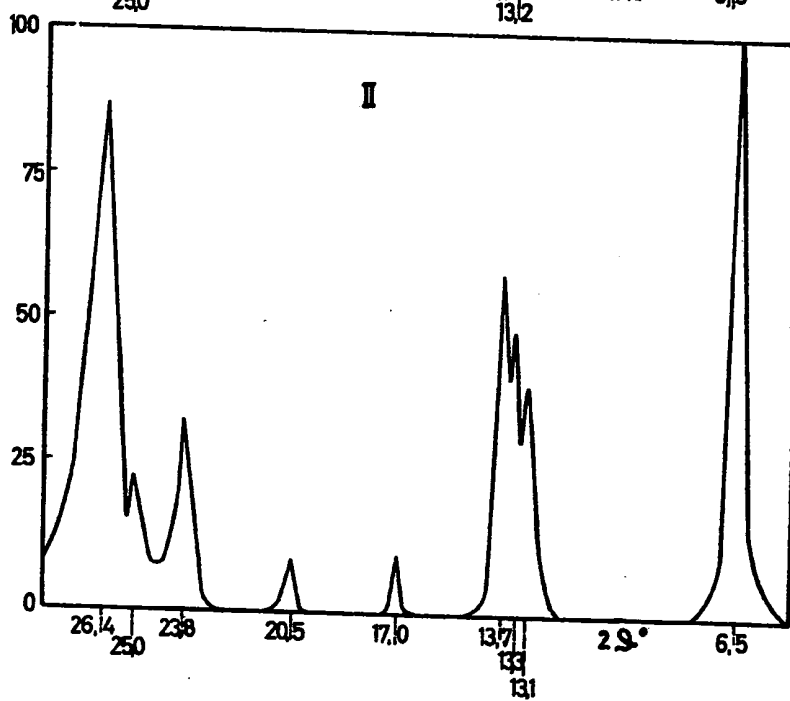
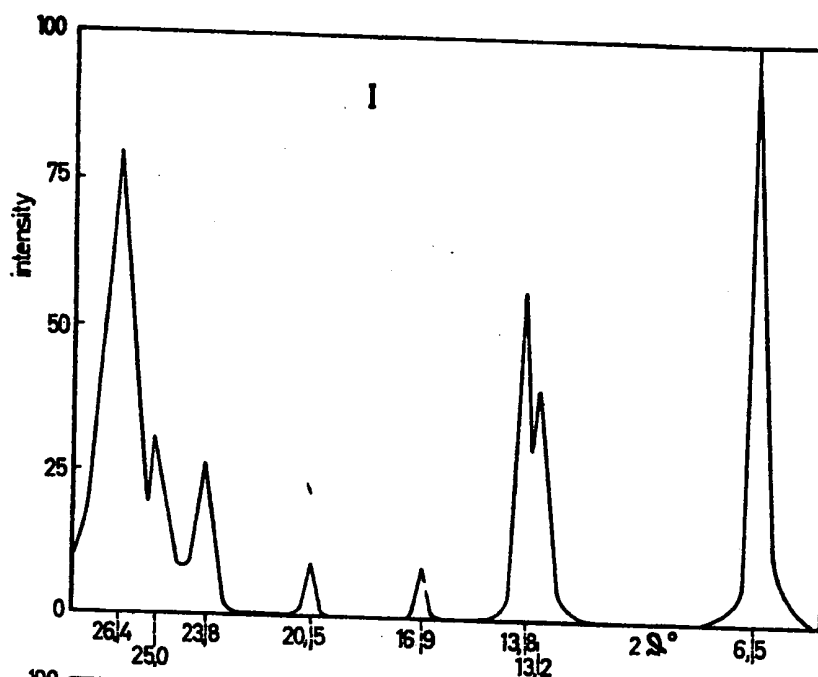
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Chartered Patent Agents,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

945.675 COMPLETE SPECIFICATION

I SHEET

This drawing is a reproduction of the Original on a reduced scale.



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)